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Microscopic Examination of the Corroded Hagan Container Used to Store Molten Salt Extraction Residue XBPS333

Joshua Narlesky, Kennard Wilson and Elizabeth Kelly

Abstract

A microscopic examination was performed on a Hagan container after corrosion and a white powder were found on the outside surface of the lid and filter cover while in storage in the vault. The inside surfaces of the container were covered by a wipeable brown coating. The coating was removed and portions of the container were sectioned and imaged with optical microscopy. General corrosion was found throughout the inside of the container, and pitting corrosion was observed in several locations on the lid and sidewall. This report describes the type and extent of the corrosion observed and its impact on the storage lifetime of the container.

Introduction

In 2016, a Hagan container was found to have a white powder and rust covering outside surface of the filter cover and part of the lid during an In-Service Inspection in the vault [1]. The item, XBPS333 had been in storage for 8.1 years and consisted of 978 g-net of material containing 80 g of plutonium and 23 g of americium. The material form is residue from the molten salt extraction (MSE) process and referred to as an MSE salt. These materials are known to contain hygroscopic chloride salt compounds including MgCl_2 , PuCl_3 , and possibly AmCl_3 . In vented containers, the stored materials have the potential to adsorb moisture from the atmosphere. Prolonged exposure to relative humidity above 30% (considered an off-normal event) could lead to hydration and deliquescence of the chloride salt compounds, increasing the likelihood for corrosion of the inner packaging in contact with the stored materials and gas-phase corrosion due to the generation of corrosive gas species.



Figure 1. Image showing the condition of the XBPS333 Hagan container in the vault [1].

Immediate concerns for radiological contamination and the identity of the white substance were resolved by taking radiological smears around the container and analytical samples of the white powder deposited on the surface of the container lid and on the window of the storage location. No contamination was found on the external surfaces of the container. The white deposits on the container were determined to be ammonium chloride, and the deposits on the vault window were found to be lead chloride. The ammonium chloride and lead chloride were presumed to be the products of reactions with hydrogen chloride gas, produced by radiolysis of the PVC bagout bag and possibly by radiolysis of hydrated chloride salts in the material matrix.

Due to concerns regarding the condition of the inner packaging and the likelihood that the inner surfaces of the Hagan container may have radioactive contamination, the container was introduced into the glovebox line for opening and repackaging. The container was opened, and images were taken to document the configuration and condition of the inner packaging. The images, which are displayed in Figure 1, show that inner package consisted of a taped slip lid container inside two bagout bags. The material was in the form of large chunks with a small amount of finer grained material on the bottom. The innermost bagout bag was completely black, brittle, and adhered to the container. The outer bagout bag was yellow to black colored and severely degraded. The inner surfaces of the Hagan had the appearance of being heavily rusted, and a gummy residue remained on portions of the inner surface of the Hagan that were in contact with the bag. The coating was found to be wipeable and was removed from some of the surface with a wet rag.

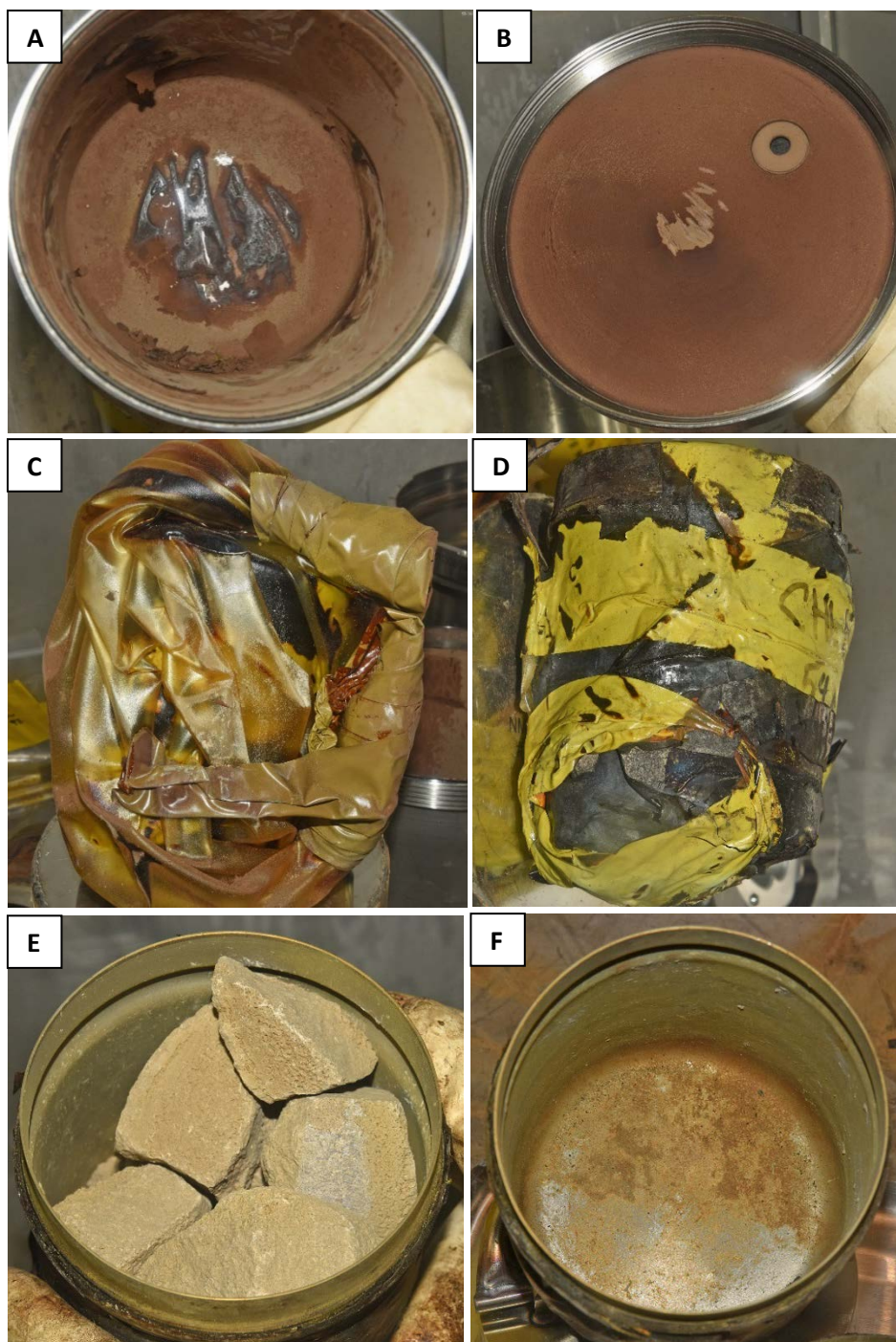


Figure 2. Condition and packaging configuration of the XBPS333 Hagan: (A) inside of outer container, (B) inside of lid, (C) outer bagout bag, (D) inner bagout bag, (E) inner container holding the chunks of material, and (F) inside of inner container.

This report describes the type and extent of the corrosion observed on the container. Specimens of the XBPS333 container were obtained from various regions of the container and examined using optical microscopy. A specimen of an unused Hagan container was also obtained and imaged for comparison purposes. The features presumed to have resulted from corrosion during storage were analyzed to determine the impact of the corrosion on the container lifetime.

Methods

Three representative specimens were obtained from the Hagan container by cutting with a low-speed trim saw. The approximate locations of the specimens are shown in Figure 3. Specimen 1 was obtained from the container sidewall near the bottom of the container. Specimen 2 was obtained from the container bottom. Specimen 3 was obtained from the container sidewall near the top of the container and included the collar. One specimen of an unused Hagan container was also obtained in the same location as Specimen 3. All three specimens were cleaned by placing each in a beaker of 2M nitric acid inside an ultrasonic cleaner for 30 minutes. After cleaning with nitric acid, the specimens were placed in a beaker of deionized (DI) water inside the ultrasonic cleaner for two minutes. The specimens were then air dried and imaged with a macroscopic camera. The remainder of the container and lid were cleaned by wiping with DI water on a wet cloth.



Figure 3. Approximate locations of the specimens obtained from the XBPS333 Hagan container.

Microscopic images were obtained with an Olympus optical microscope inside the glovebox. The microscope is fitted with a camera that transmits images to a computer. The microscope has objectives for 5X, 10X, 20X, 50X and 80X magnification. The software program includes a calibration to provide horizontal measurements. Estimates of depth were determined using the ratio of number of turns used to raise or lower the stage a known distance.

Results

Post Cleaning Images

To control for the effects of the cleaning process, the specimen from the unused Hagan was cleaned with 2M nitric acid, rinsed in DI water, and air dried. An image showing the condition of the unused Hagan specimen after cleaning is presented in Figure 6. No changes were observed in the appearance of the surfaces at the macroscopic level. The coloration and finish of the sidewall outside of the weld region were consistent throughout the specimen.

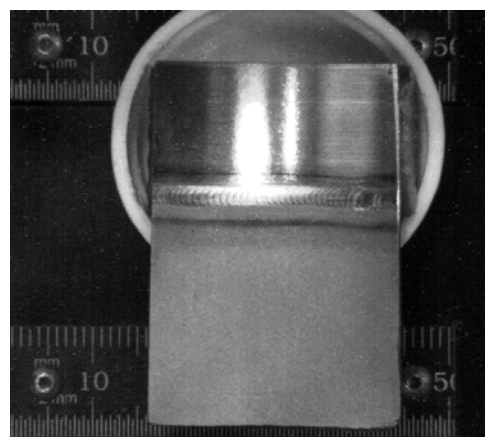


Figure 4. Image showing the Inside surfaces of the unused Hagan container.

Images showing the condition of the XBPS333 Hagan specimens after cleaning are presented in Figures 5 and 6 below. The brown coating was removed from all of the XBPS333 specimens. Comparing the surfaces of the unused Hagan with the XBPS333 Hagan we found three major differences resulting from corrosion that occurred during storage. First, areas of staining or an adherent coating remained on the inside surfaces of XBPS333 Hagan (indicated by yellow arrows in Figures 5B and 6B). Second, the collar of the XBPS333 Hagan had an uneven finish with both shiny and dull areas. Third, the weld of the XBPS333 Hagan had a dull finish; whereas, the weld of the unused Hagan had a shiny finish.

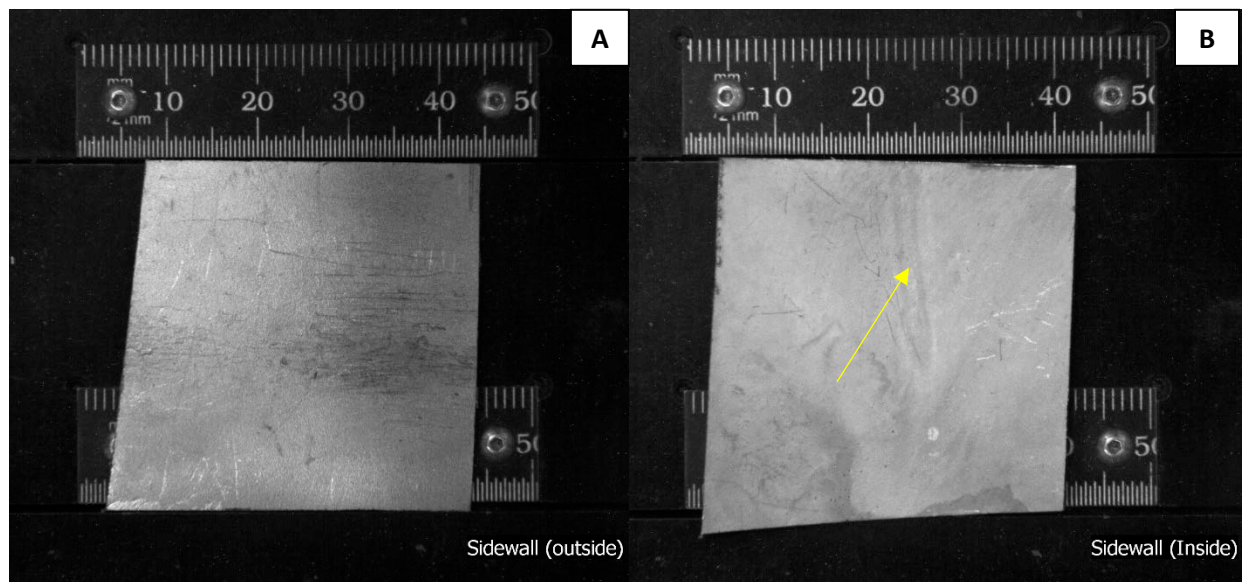


Figure 5. Images showing the outside (A) and inside (B) surfaces of the XBPS333 Hagan sidewall (Specimen 1) after cleaning. The yellow arrow shows an area of staining possibly due to adherence of the bagout bag to the container wall.

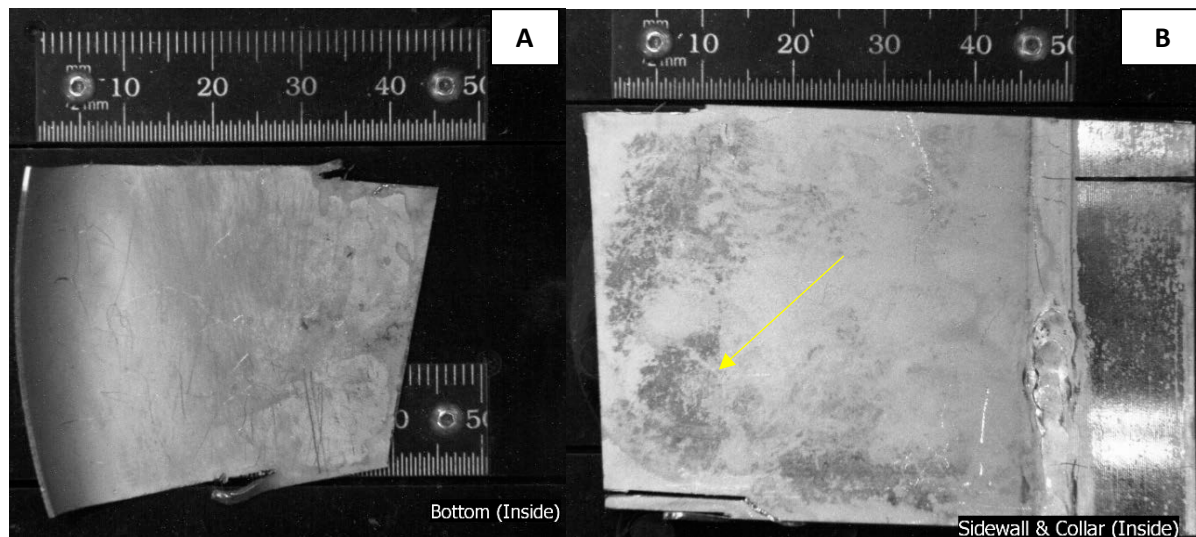


Figure 6. Images showing the inside surface of the bottom (Specimen 2) (A) and the inside surface of sidewall (Specimen 3) (B) of the XBPS333 Hagan after cleaning.

The XBPS333 Hagan lid was cleaned by wiping with DI water on a wet cloth. Images of the lid after cleaning are shown in Figure 7. The brown coating was completely removed from the lid. Under the coating, the lid had a dull finish except for areas that were protected by the O-ring seal. The difference between these areas is shown in Figure 7B.

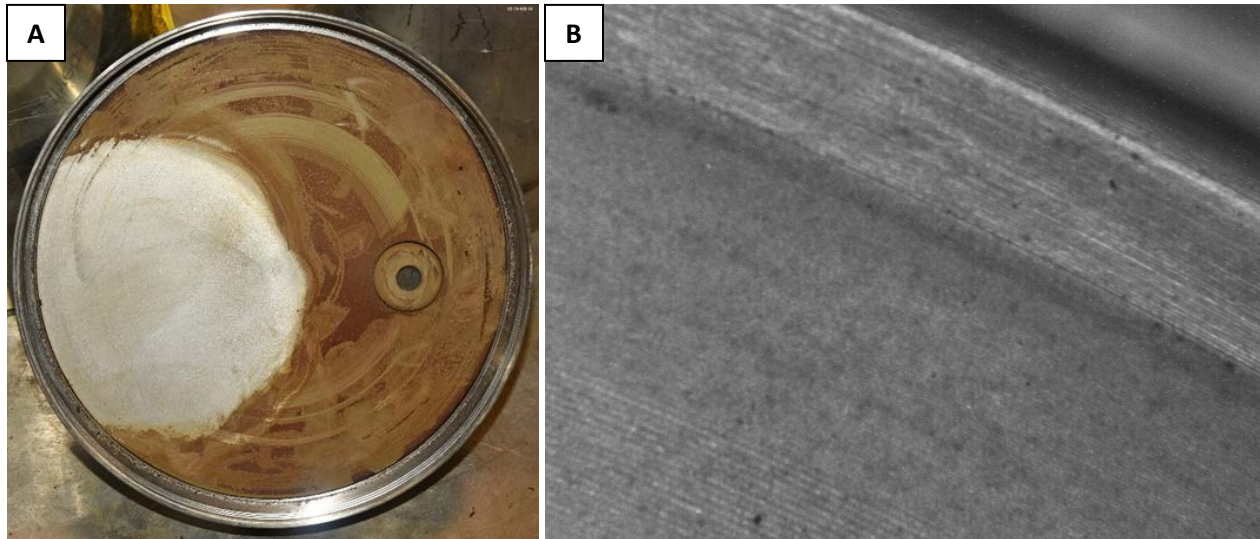


Figure 7. Removal of the wipeable coating from a portion of the XBPS333 Hagan container lid (A) and macroscopic image showing the difference in surfaces between areas of the lid protected (shiny) by the sealing surface and those exposed to the inside of the container (dull) (B).

The XBPS333 Hagan body was cleaned by wiping with DI water on a wet cloth. An image of the container body after cleaning is shown in Figure 8. Portions of the degraded bagout bag remained on the surface as well as large areas of staining.



Figure 8. Inside surfaces of the XBPS333 Hagan after cleaning with a wet cloth.

Microscopic Images: Unused Hagan, Top of Sidewall

Representative microscopic images of the inside surfaces of the unused Hagan specimen were obtained in the sidewall, weld, and collar regions at 50X magnification. Additionally, one microscopic image was obtained for outside surface of the sidewall at the same magnification. The microscopic images are shown in Figure 9. The inside surface of the sidewall was characterized by an uneven surface showing a series of irregular features resembling ridges and valleys indicated by yellow arrows in Figure 9A. The weld region appeared to have a dimpled surface throughout with scratches running through the region. The collar was characterized by the circumferential machine marks (shown as vertical lines in Figure 9C). No pits or cracks were observed in any of the regions.

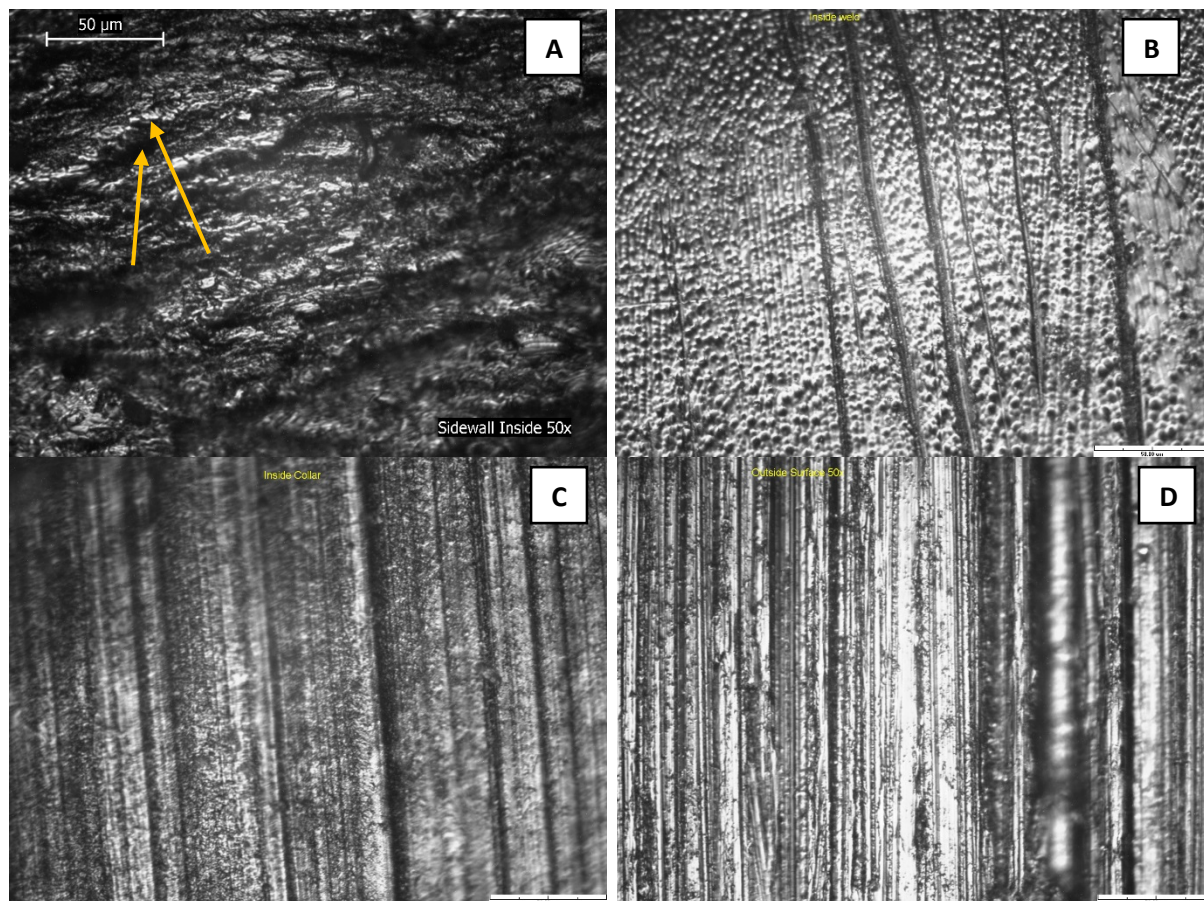


Figure 9. Microscopic images of the unused Hagan container imaged at 50X magnification before cleaning. (A) Inside sidewall below weld, (B) Inside sidewall at the middle of the weld, (C) Inside collar, (D) Outside sidewall. (The length of the scale bar at the bottom-right of each image represents 50 microns).

An additional set of microscopic images of the inside surfaces of the unused Hagan after cleaning were obtained in the same regions. These images are shown in Figure 10. The surfaces appear to be unaffected by the cleaning solutions, based on the similarity of the features in each region both before and after cleaning.

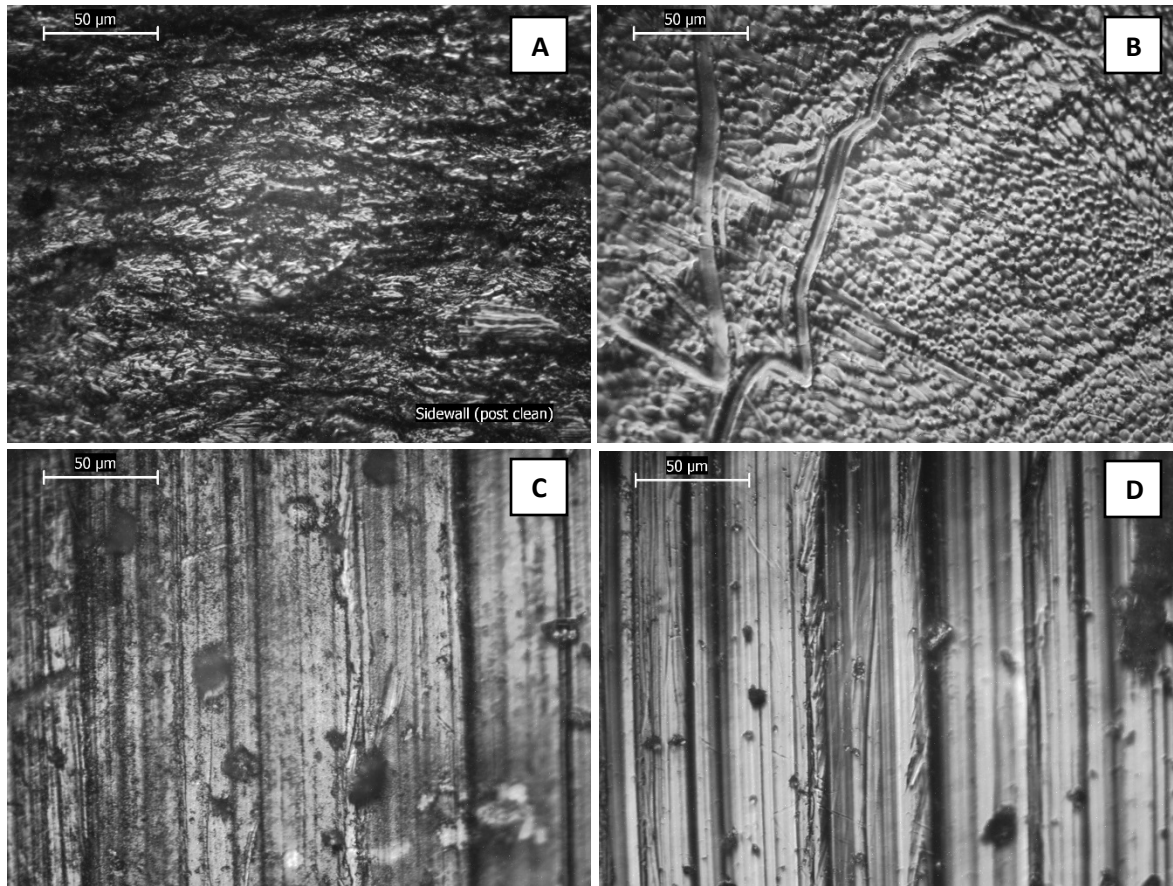


Figure 10. Microscopic images of the unused Hagan container imaged at 50X magnification after cleaning. (A) Inside sidewall below weld, (B) Inside sidewall at the middle of the weld, (C) Inside collar, (D) Outside sidewall. (The length of the scale bar at the bottom-right of each image represents 50 microns).

Microscopic Images: XBPS333 Hagan, Bottom of Sidewall (Specimen 1)

Microscopic images were taken using 50X magnification in various regions of specimen 1, taken from the bottom of the XBPS333 Hagan. Comparing sidewall surfaces of the XBPS333 Hagan and unused Hagan (Figures 11 and 10A, respectively), it is evident that the ridges and valleys that cover the surface of the unused Hagan were not present anywhere in the XBPS333 Hagan specimen. It is unclear whether the ridges and valleys were eroded by general corrosion or whether the difference is due to the fabrication process.

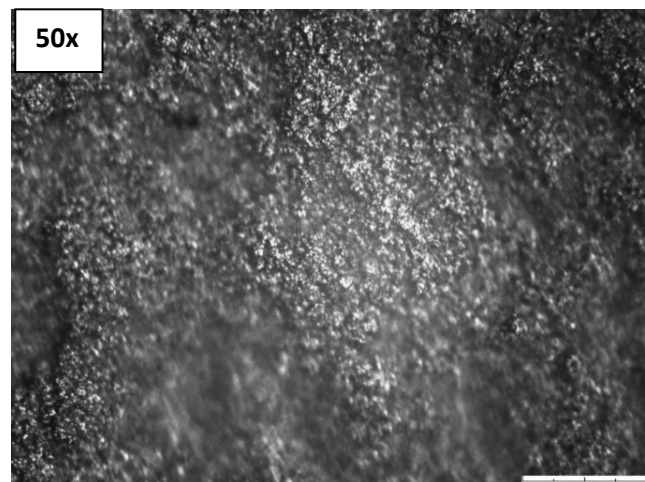


Figure 11. Inside surface of specimen 1 imaged at 50X magnification. (The length of the scale bar at the bottom-right represents 50 microns).

Isolated areas containing corrosion pits were observed on this specimen. The highest concentration of pits was observed in the immediate area surrounding the staining as indicated by the yellow arrow in Figure 5B. The pit diameters were mostly on the order of 5 to 30 microns, but some larger pits and agglomerated pits were observed. Figure 12A shows several pits observed in this region. Pit 1 was the largest pit observed at approximately 105 microns in diameter and approximately 40 microns deep. Pits 2 and 3 are approximately 30 microns in diameter. The depth of pit 3 is approximately 30 microns. The depth of pit 2 was not estimated. Figure 12B shows the variety of pit shapes ranging from small and circular on the far left of the image to long and agglomerated in the center and right side of the image. (The light colored features indicated by arrows are below the surface.) The depths of the features in Figure 12B were on the order of 10 microns or less. Figure 12C shows a hemispherical pit (pit 4) indicated by the yellow arrow. The diameter measured 26 microns, and its depth was between 10 and 20 microns. Figure 12D shows an area densely populated with relatively small pits on the order of 20 microns in diameter.

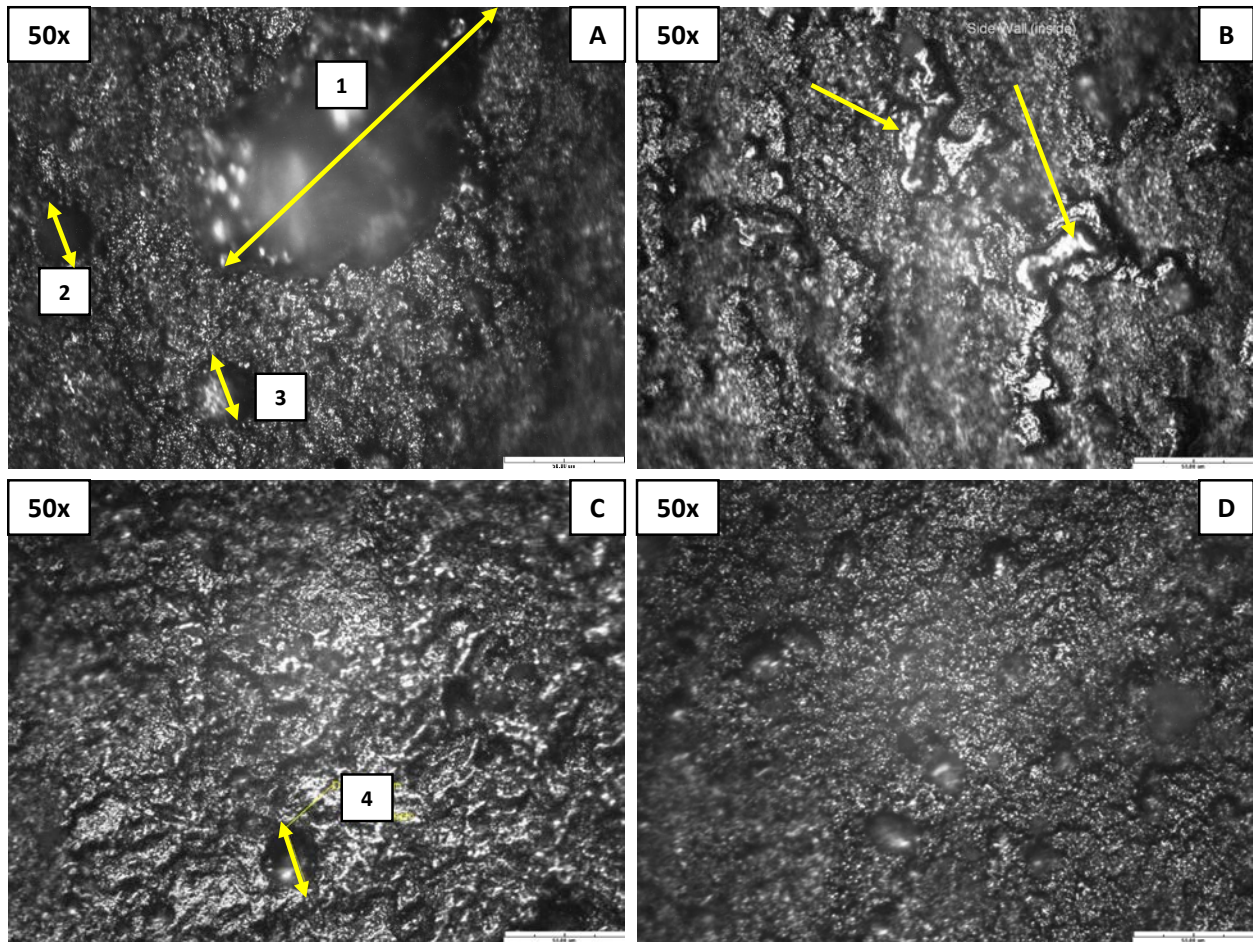


Figure 12. Areas of the specimen 1 containing corrosion pits imaged at 50X magnification. (The length of the scale bar at the bottom-right of each image represents 50 microns).

Microscopic Images: XBPS333 Hagan, Container Bottom (Specimen 2)

The inside surface of specimen 2 taken from the bottom of the XBPS333 Hagan was scanned for features using 50X magnification. A microscopic image representing this region was obtained and is shown in Figure 13 and shows that the bottom of the container has a similar appearance to that of the sidewall specimen (Figure 12). The ridges and valleys observed in the unused Hagan specimen are absent from this specimen. Some areas were found to have small, round, shallow features, which have the appearance of shallow pits. These features, on the order of 10 to 20 microns in diameter, were the largest features observed in this specimen.

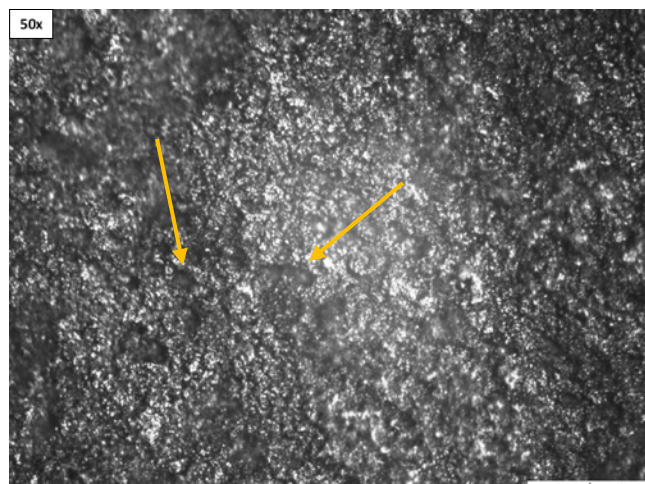


Figure 13. Inside surface of specimen 2 imaged at 50X magnification. Yellow arrows indicate round features resembling shallow pits. (The length of the scale bar at the bottom-right represents 50 microns).

Microscopic Images: XBPS333 Hagan, Top of Sidewall (Specimen 3)

The inside surface of the specimen 3 taken from the top of the XBPS333 Hagan was scanned for features using 50X magnification. The surfaces of the sidewall below the weld (Figure 14A) have similar appearance to the container specimens 1 and 2 from the bottom and sidewall. No pits or cracks were observed in the sidewall or weld regions. The ridges and valleys observed in the unused Hagan specimen were not observed in this specimen. The weld region in the XBPS333 Hagan (Figure 14B) had a similar appearance to sidewall surfaces elsewhere in the XBPS333 container rather than the weld surface in the unused Hagan (Figure 10B). It is unclear whether the difference in the surfaces between the unused Hagan and the XBPS333 Hagan are the result of corrosion or differences in the fabrication process.

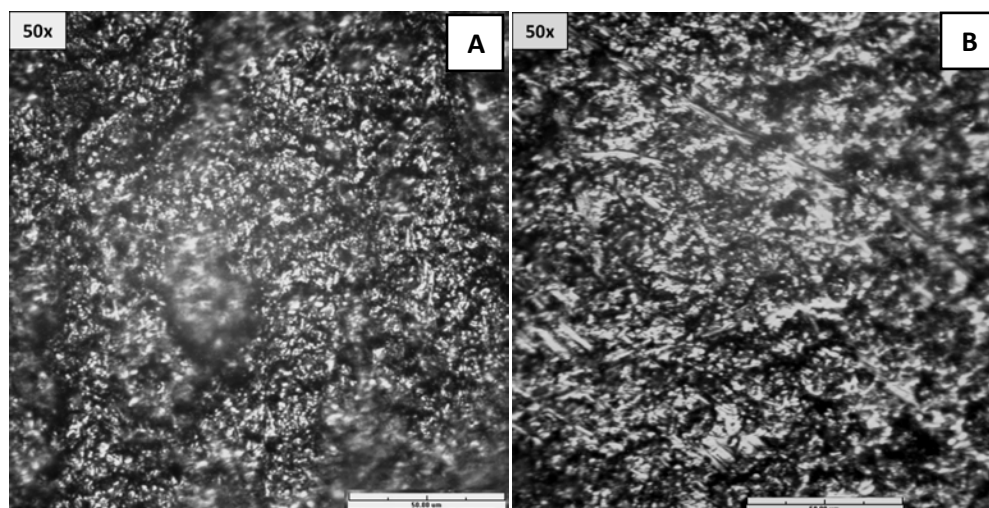


Figure 14. Inside surfaces of specimen 3 imaged at 50X magnification. (A) Inside sidewall below weld, (B) Inside sidewall at the middle of the weld. (The length of the scale bar at the bottom-right of each image represents 50 microns).

The collar of the XBPS333 Hagan was also scanned for features using 50X magnification. The machining marks in this region are punctuated by features that are possibly areas of small, agglomerated pits or

general corrosion. Those features, which appear as dark areas at the bottom center of Figure 15 were not observed on the unused Hagan.

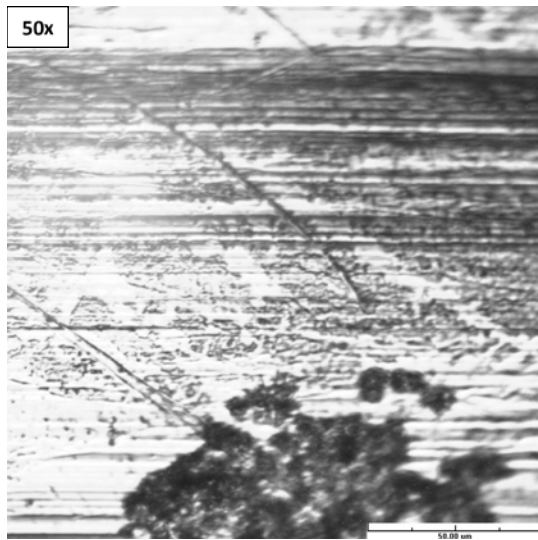


Figure 15. Inside surfaces of specimen 3 at the collar of the XBPS333 Hagan imaged at 50X magnification. (The length of the scale bar at the bottom-right represents 50 microns).

Microscopic Images: XBPS333 Hagan, Lid

Microscopic images of the cleaned, inside surface of the XBPS333 Hagan lid were obtained at 80X magnification. The microscopic image is shown in Figure 16. Light colored regions indicate areas of clean metal bearing its machining marks, which are punctuated by dark irregular-shaped circular-shaped features resembling corrosion pits. The size of the circular pits ranged from approximately 5 to 15 microns in diameter. All of the features were shallow (less than 10 microns).

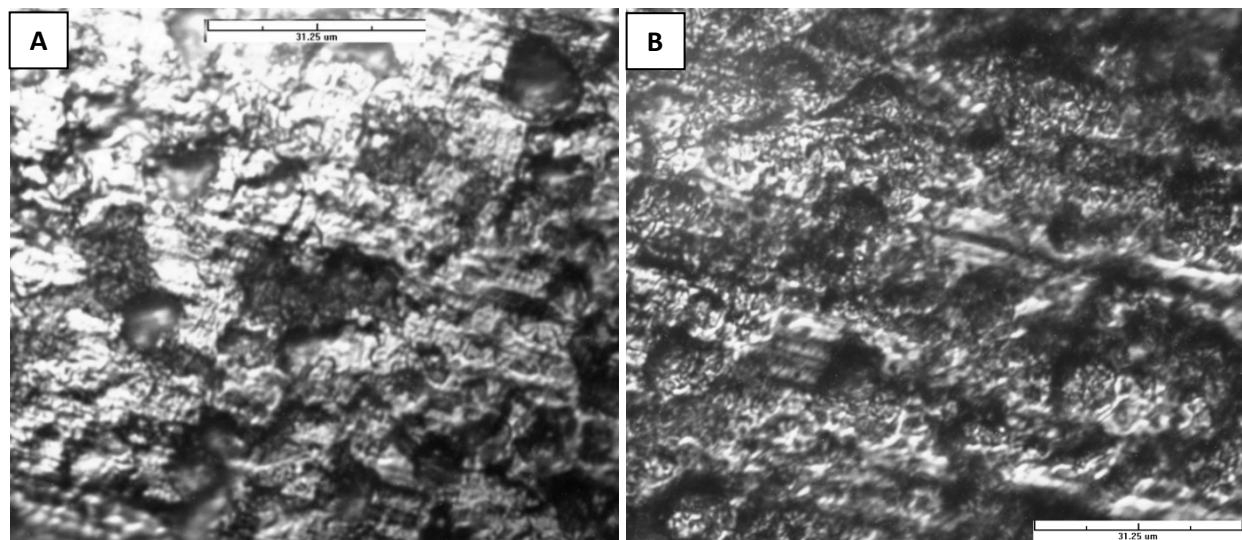


Figure 16. Inside surface of the XBPS333 Hagan lid imaged at 80X magnification. (The length of the scale bar at the bottom-right represents 31.25 microns).

Discussion

The materials of construction for Hagan and SAVY 4000 containers are stainless steel types 304L and 316L, respectively. These materials are considered corrosion-resistant materials due to the presence of chromium and nickel, which help the materials to form passivation layers [2]. Stainless steel type 316L is considered more corrosion resistant than type 304L due to the added molybdenum. Exposure to chloride solutions can break down the passivation layer and lead to corrosion. The severity of corrosion depends on the form of the chloride, the pH, and the relative humidity. General corrosion occurs under extreme acidic or alkaline conditions. This type of corrosion generally occurs at a low rate and is not considered life-limiting. Localized corrosion, such as pitting and stress corrosion cracking, may occur in the pH range of 2 to 12 and leads to much higher corrosion rates.

Hydrogen chloride gas and solution causes uniform or general corrosion on both 304L and 316L stainless steels at room temperature [3,4]. Under dry conditions, the resistance to general corrosion on both 304L and 316L stainless steels is considered good at room temperature and poor at 400C [5]. The presence of water vapor increases the severity of the corrosion by hydrogen chloride gas at lower temperature [3]. Studies with stainless steel type 304L teardrop specimens exposed to 0.15 Torr hydrogen chloride gas at 31, 48, and 68% relative humidity at room temperature have demonstrated that corrosion is more aggressive at higher relative humidity causing pitting as well as general corrosion [6]. In addition, severe pitting was observed in a study in which stainless steel types 304 and 316 were exposed to fumes from a tank containing a 19% solution of hydrochloric acid at temperatures ranging from 70 to 82°C. The general corrosion rates for stainless steel types 304 and 316 in this study were found to be 0.22 and 0.18 mm/year, respectively. The relative humidity above a 19% hydrochloric acid solution at temperatures between 70 to 82°C is approximately 63%, and the vapor pressure of hydrogen chloride was between 8 and 11 Torr. The highest general corrosion rates occur under the direct exposure to hydrochloric acid solutions, where the corrosion rates of stainless steel types 304 and 316 may both exceed 0.75 mm/year [4].

The conditions described in the above studies are much more extreme than the conditions inside Hagan and SAVY 4000 storage containers. Under normal packaging and storage conditions, Hagan and SAVY 4000 containers would have much lower concentrations of hydrogen chloride gas and water vapor. The hydrogen chloride gas produced inside the containers is continually vented, and the water vapor inside the container is in equilibrium with the water vapor in the room air. The relative humidity in the facility is controlled and is typically less than 35% in all rooms of the vault [7]. Additionally, the radiative self-heating of the container due to the plutonium isotopes would further lower the relative humidity inside the container with respect to the room, mitigating the effect of the moisture. The Hagan container packaged with XBPS333 had some of the most severe general corrosion observed to date in a storage container [1]. This container had a large source of HCl due to the inner container being placed inside two bagout bags. For most of the storage period, the relative humidity inside this container would have been slightly lower than that of the room, based on the measured material temperature of 37°C. However, the storage location experienced a high-humidity event that may have temporarily increased the relative humidity inside the container leading to the general corrosion and pitting that were observed.

The maximum pit depth observed in the XBPS333 Hagan container was 40 microns. Assuming that the conditions in the container remain the same during the storage lifetime, a growth model can be used to

estimate the depth of a pit over time and the time required for the pit to penetrate the container wall. A power law for pit depth growth as a function of time (t) is often given by $depth(t) = \beta t^b$. [8, 9, 10, 11]. The value of the parameter b is generally taken to be ≤ 0.5 . Experiments by Duque using teardrop data support this growth model with $b = 0.5$ within the experimental uncertainty bounds [12]. A more conservative assumption and one that is unphysical is to use $b = 1$. Assuming 40 microns is the maximum pit depth for all pits, the model with $b = 0.5$ results in a time to penetration of 2,903 years, and the conservative model with $b = 1$ results in a time to penetration of 152 years. Assuming 40 microns is the maximum pit depth is reasonable given that this pit comes from the area where the bagout bag touches the container, and it is this area where the most pitting is observed. Other areas do not show this extent of pitting. It would require a very large pit after eight years to result in a through-wall penetration in ten years (greater than a millimeter in diameter). Such a pit would not have been missed. In addition, it is unlikely that the conditions for corrosion inside the container will remain the same over time because the source of HCl gas will eventually be depleted by radiolysis. Therefore, it is unlikely that the pitting observed to date would impact the storage lifetime.

Conclusion

Optical microscopy was performed on cleaned specimens of the lid and body of XBPS333. The microscopic images obtained from the XBPS333 Hagan container specimens were compared with images obtained from specimens of an unused Hagan container using the same magnification. Images of the unused Hagan container specimens before and after cleaning show uniform surfaces within each of the sidewall, weld, and collar regions. Microscopic images show that the surface does not change as a result of the cleaning process. If one assumes that the fabrication process was the same for both containers, then differences between the XBPS333 and the unused Hagan container may be attributed to corrosion.

The main features observed on the XBPS333 Hagan at the macroscopic level were staining and changes in surface finish. On the microscopic level, the main features were general corrosion and pitting. No evidence of cracking was observed. The inside surfaces of the collar region and lid region are machined, and corroded areas are easily distinguishable from the native surface due to the machining marks. Here, isolated areas of general corrosion were found to be present throughout the collar. The lid also appeared to have general corrosion and corrosion pits (5 to 15 microns in diameter) in areas exposed to the inner package. The depth of features observed in the lid and collar regions was estimated to be less than 10 microns. The inside sidewall surfaces of both the XBPS333 Hagan and the unused Hagan have a rough appearance throughout; therefore, and the changes in thickness of the side wall due to general corrosion cannot be determined because it is not possible to compare areas that experienced general corrosion with an unexposed native surface on the same specimen. However, the reduction in thickness is expected to be small with respect to the depth corrosion pits found in the same regions. The diameters of pits found on the sidewall from 5 to 105 microns. These features were associated with areas that were stained due to contact with the bagout bag during storage. The maximum diameter of any circular pit observed was 105 microns, and the maximum depth of the largest pit was 40 microns.

The sidewall thickness of Hagan and SAVY 4000 containers is nominally 30 thousandths of an inch. Based on the depth of the largest pit observed (40 microns), the maximum penetration of the sidewall was approximately 5% after 8 years. SAVY 4000 container bodies being constructed from stainless steel type 316L steel have lower rates of corrosion under some conditions and are less likely to undergo cracking

due to annealing. The most conservative pit growth model estimates a time to penetration of 152 years for a 40 micron pit, which shows that the pitting observed to date will not impact the storage lifetime of the Hagan or SAVY 4000 containers.

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